Heteropolynuclear Sodium(I) Lead(II) Complex: Crystal and Molecular Structure of a Novel 3-D Polymer, $[(\text{en})\text{Pb}(\mu_3\text{-ONO})_2\text{Na}(\mu_3\text{-ONO})_2\text{Na}(\mu\text{-O}_2\text{ClO}_2)\text{Na}]_n$

by **Ali Morsali***[a]) and **Xiao-Ming Chen**[b])

[a]) Department of Chemistry, School of Sciences, Tarbiat Modarres University, P.O. Box 14155-4838, Tehran, Iran (e-mail: morsali_a@yahoo.com)

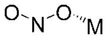
[b]) School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China

A novel 3D polymeric heteropolynuclear sodium(I) lead(II) complex containing different ligands, $[\text{NaPb}(\text{ClO}_4)(\text{en})(\text{NO}_2)_2]$ was synthesized and characterized by elemental analysis and IR, and ^{1}H-, ^{13}C-, and ^{207}Pb-NMR spectroscopy. The single-crystal X-ray data of $[\text{NaPb}(\text{ClO}_4)(\text{en})(\text{NO}_2)_2]_n$ established that the complex is a three-dimensional polymer, $[(\text{en})\text{Pb}(\mu_3\text{-ONO})_2\text{Na}(\mu_3\text{-ONO})_2\text{Na}(\mu\text{-O}_2\text{ClO}_2)\text{Na}]_n$. The Pb and Na atoms have four- and eight-coordinate geometry, respectively. The lone pair of electrons at the Pb^{II} atom is 'stereochemically active'.

1. Introduction. – The concept of crystal engineering has provided numerous examples [1][2] of rationally designed one-, two-, and three-dimensional polymeric structures. Of particular potential interest to inclusion chemistry are 2D and 3D coordination polymers, which, in principle at last, can be designed to have a very specific cavity size and type. Moreover, The 3D networks are usually generated *via* self-assembly of tetrahedral or octahedral nodes. Tetrahedral nodes are disposed to generate diamond-like architectures, whereas octahedral nodes are expected to afford octahedral networks [1]. The rigid spacer ligands such as 4,4′-bipyridine and flexible ligands such as 1,2-bis(4-pyridyl)ethane (=4,4′-(ethane-2,1-diyl)bis[pyridine] are widely used for the synthesis of coordination polymers [1–8]. On the other hand, despite the well-established coordination polymers, available structural information about supramolecular compounds containing the bridging nitrito ligand is relatively scarce.

The nitrito ligand is an ambidentate ligand and can coordinate metal ions *via* both the N- and O-atoms. This anion is also a multi-coordination-modes ligand that acts in the monodentate coordination that may occur either through the O-atom to give a nitrito-κO (=nitrito) complex **1**, or through the N-atom to give a nitrito-κN (=nitro) complex **2**. Bidentate coordination is known to take place either by chelation (see **3**) or by forming a bridge such as in **4**–**6** [9–13]. However, in the three latter forms **4**–**6**, the compounds containing the nitrito-κO ligand can be polymeric. For these reasons, there are a great variety of complexes containing the nitrito ligand.

However, it is of interest to build and structurally design new polymeric species of heteropolynuclear complexes, known as coordination polymers, with two different metal ions that are both bridged by the nitrito ligand (see **6**), and to modify their architectures to control their physical properties. We report here the preparation, full



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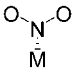

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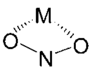

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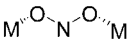

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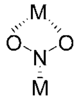

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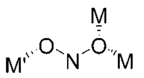

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structural characterization, and crystal packing of $[(\text{en})\text{Pb}(\mu_3\text{-ONO})_2\text{Na}(\mu_3\text{-ONO})_2\text{Na}(\mu\text{-O}_2\text{ClO}_2)\text{Na}]_n$ as a new 3D polymeric system.

2. Experimental. – *(Ethane-1,2-diamine-κN,κN′)bis(μ_3-nitrito-κO:κO′:κO′)(μ-perchlorato-κO,κO:κO′,κO′)leadsodium* ($[\text{NaPb}(\text{ClO}_4)(\text{en})(\text{NO}_2)_2]_n$. The complex was prepared by the branch-tube method: ethane-1,2-diamine (en; 0.12 g, 2 mmol) was placed in one arm of the branched tube, and a mixture of lead(II) acetate (0.72 g, 2 mmol), sodium perchlorate (0.246 g, 2 mmol), and sodium nitrite (0.138 g, 2 mmol) in the other. MeOH was carefully added to fill both arms, the tube sealed, and the ligand-containing arm immersed in a bath at 60°, while the other was at r.t. After 12 days, yellow crystals, which had deposited in the cooler arm, were filtered off, washed with acetone and Et_2O, and air-dried: 0.192 g (40%) of $\text{NaPb}(\text{ClO}_4)(\text{en})(\text{NO}_2)_2]_n$. M.P. 250°. IR ($\text{cm}^{-1}$; selected bands): 720*s*, 805*s*, 1110*vs*, 1225*vs*, 1585*s*, 2980*w*, 3235*s*. ^1H-NMR ((D_6)DMSO; δ): 3.20 (*s*, 4 H), 3.50 (*s*, 4 H). $^{13}\text{C}\{^1\text{H}\}$-NMR (($\text{D}_6$)DMSO; δ): 42.60. ^{207}Pb-NMR ((D_6)DMSO; δ): –2150.44. Anal. calc. for $\text{C}_2\text{H}_8\text{ClN}_4\text{NaO}_8\text{Pb}$. C 4.98, H 1.66, N 11.61, Pb 43.15; found: C 5.10, H 1.30, N 11.70, Pb 44.00.

3. Results and Discussion. – The $[\text{NaPb}(\text{ClO}_4)(\text{en})(\text{NO}_2)_2]_n$ complex was characterized by its IR and NMR spectra and its elemental analysis (see *Experimental*). Single-crystal X-ray-diffraction analysis of the complex was carried out (*Fig. 1*)1). The crystal structure of $[\text{NaPb}(\text{ClO}_4)(\text{en})(\text{NO}_2)_2]_n$ consists of three-dimensional polymeric units of $[(\text{en})\text{Pb}(\mu_3\text{-ONO})_2\text{Na}(\mu_3\text{-ONO})_2\text{Na}(\mu\text{-O}_2\text{ClO}_2)\text{Na}]$. Each Pb-atom is chelated by two N-atoms of the en ligand with Pb–N distances of 2.397 and 2.402 Å, and by two O-atoms of two nitrito ligands with Pb–O distances of 2.604 and 2.629 Å. The coordination number of the Pb-atoms is four (two of en ligand, two of nitrito ligands).

The O-atoms of nitrito and perchlorato ligands are linked to different Na-atoms. Each Na-atom is linked by the O-atoms of nitrito ligands with distances of Na–O(8)#*1* 2.363, Na–O(5) 2.366, Na–O(6)#*2* 2.369, and Na–O(7)#*3* 2.400 Å, and also by the O-atoms of perchlorato ligands with distances of Na–O(3)#*4* 2.634, Na–O(2)#*5* 2.777, Na–O(4)#*5* 2.918, and Na–O(1)#*4* 2.949 Å. The coordination number of the Na-atoms is eight (four of nitrito and four of perchlorato ligands) and both nitrito and perchlorato ligands bridge the Na-atoms and produce the polymer units in the solid state. The

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1) Crystal data: $\text{C}_2\text{H}_8\text{ClN}_4\text{NaO}_8\text{Pb}$, $M = 479.72$, crystal dimension 0.28 × 0.16 × 0.14 mm; orthorhombic, space group *P*2(1)2(1)2(1); $a = 8.6110(11)$, $b = 9.5338(12)$, $c = 13.5422(17)$ Å, $V = 1111.8(2)$ Å^3, D_c (Z = 4 f.u.) = 2.854 Mg/m^3, *F*(000) 872. $R(wR) = 0.0317(0.0658)$ for reflections with $I > 2\sigma(I)$. All bond lengths and angles, coordinates, and displacement parameters have been deposited at the *Cambridge Crystallography Data Centre*. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB21EZ, UK on request, quoting the deposition No. 230242.

Fig. 1. *ORTEP Diagram of* $[NaPb(ClO_4)(en)(NO_2)_2]_n$. Selected bond lengths [Å]: Na–O(8)#*1* 2.363(6), Na–O(5) 2.366(5), Na–O(6)#*2* 2.369(6), Na–O(7)#*3* 2.400(5), Na–O(3)#*4* 2.634(8), Na–O(2)#*5* 2.777(7), Na–O(4)#*5* 2.918(8), Na–O(1)#*4* 2.949(8), Pb(1)–N(2) 2.397(6), Pb(1)–N(1) 2.402(6), Pb(1)–O(5) 2.604(5), Pb(1)–O(7) 2.629(5). Selected bond angles [°]: O(8)#*1*–Na-O(5) 92.06(19), O(8)#*1*–Na-O(6)#*2* 154.7(3), O(5)-Na–O(6)#*2* 90.1(2), O(8)#*1*–Na-O(7)#*3* 87.4(2), O(5)–Na–O(7)#*3* 163.0(2), O(6)#*2*–Na–O(7)#*3* 97.6(2), O(8)#*1*–Na–O(3)#*4* 126.8(2), O(5)–Na–O(3)#*4* 84.6(2), O(6)#*2*–Na–O(3)#*4* 78.6(2), O(7)#*3*–Na–O(3)#*4* 82.2(2), O(8)#*1*–Na–O(2)#*5* 80.0(2), O(5)–Na–O(2)#*5* 77.77(19), O(6)#*2*–Na–O(2)#*5* 75.8(2), O(7)#*3*–Na–O(2)#*5* 118.8(2), O(3)#*4*–Na–O(2)#*5* 148.7(2), O(8)#*1*–Na–O(4)#*5* 79.62(19), O(5)–Na–O(4)#*5* 126.1(2), O(6)#*2*–Na–O(4)#*5* 78.76(19), O(7)#*3*–Na–O(4)#*5* 70.53(18), O(3)#*4*–Na–O(4)*5* 141.49(19), O(2)#*5*–Na–O(4)#*5* 48.32(17), O(8)#*1*–Na–O(1)#*4* 77.8(2), O(5)–Na–O(1)#*4* 83.87(19), O(6)#*2*–Na–O(1)#*4* 127.5(2), O(7)#*3*–Na–O(1)#*4* 79.40(19), O(3)#*4*–Na–O(1)#*4* 49.0(2), O(2)#*5*–Na–O(1)#*4* 150.51(19), O(4)#*5*–Na–O(1)#*4* 142.91(18), N(2)–Pb(1)–N(1) 73.4(2), N(2)–Pb(1)–O(5) 74.42(19), N(1)–Pb(1)–O(5) 84.24(19), N(2)–Pb(1)–O(7) 83.07(18), N(1)–Pb(1)–O(7) 75.05(19), O(5)–Pb(1)–O(7) 152.99(19). #*1:* $x-1/2, -y-1/2, -z$; #*2:* $x-1/2, -y+1/2, -z$; #*3:* $x-1, y, z$; #*4:* $x-1/2, -y-1/2, -z-1$; #*5:* $-x-1, y+1/2, -z-1/2$; #*6:* $x+1/2, -y-1/2, -z-1$; #*7:* $-x-1, y-1/2, -z-1/2$; #*8:* $x+1/2, -y+1/2, -z$; #*9:* $x+1, y, z$; #10: $x+1/2, -y-1/2, -z$.

nitrito ligands can bridge both the two Na-atoms as well as the Na- and Pb-atoms. Indeed, one of the O-atoms of this ligand is coordinated to the Pb-atom along the *b* axis (*Fig. 2,a* and *Fig. 3*) and the other O-atom is linked to two different Na-atoms along the *c* axis (*Fig. 2,a* and *Fig. 3*).

The tetradentate perchlorato ligand bridges different Na-atoms creating Na···(O_2ClO_2)···Na scaffoldings along the *a* axis (*Fig. 2,b* and *Fig. 4*). Consequently, as shown in *Fig. 3* and *Fig. 4*, these bridgings by both the nitrito ligands in two dimensions (*b* and *c* axes) and the perchlorato ligands in another dimension (*a* axis), yields infinite chains parallel to the crystallographic axes *a*, *b*, and *c* and produce a three-dimensional polymeric compound. The 3D network of the $[(en)Pb(\mu_3\text{-}ONO)_2Na(\mu_3\text{-}ONO)_2Na(\mu\text{-}O_2ClO_2)Na]_n$ complex is a novel octahedral architecture with a coordination number 8 for the Na-atoms that lie in the regular manner along the *b* axis between the four coordinated Pb-atoms with O···Pb(en)···O scaffolding.

The structure of $[NaPb(ClO_4)(en)(NO_2)_2]_n$ is interesting with respect to several features. The compound has a new rarely observed 3D framework, it is a complex containing three different ligands, and it is a heteropolynuclear complex containing two different metal ions that are both coordinated in its crystal structure.

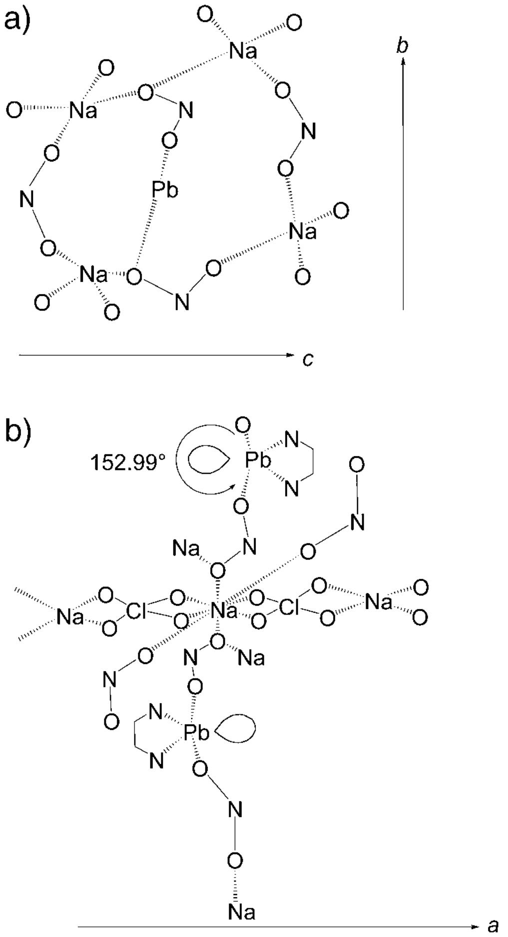

Fig. 2. *Ligand bridging* a) *in the* cb *plane and* b) *in the* ab *plane of* $[NaPb(ClCO_4)(en)(NO_2)_2]_n$

The arrangement of the en and nitrito ligands around the Pb-atom suggests a gap or hole in the coordination geometry of the Pb-atom (O(5)–Pb(1)–O(7) angle 152.99°), occupied possibly by a 'stereochemically active' lone pair of electrons at Pb^{II}. Hence, the geometry of the nearest coordination environment of each Pb-atom is probably caused by the geometrical constraints of the coordinated en and nitrito ligands and by the influence of a 'stereochemically active' lone pair of electrons in a hybrid orbital of the Pb-atom.

The possible 'stereochemical activity' of the lone pair in divalent lead compounds has recently been discussed by *Shimoni-Livny et al.* based on a thorough review of crystal data available in the *Cambridge Structural Database* (CSD) [14]. They classify lead coordination as holodirected, which refers to complexes in which the bonds to

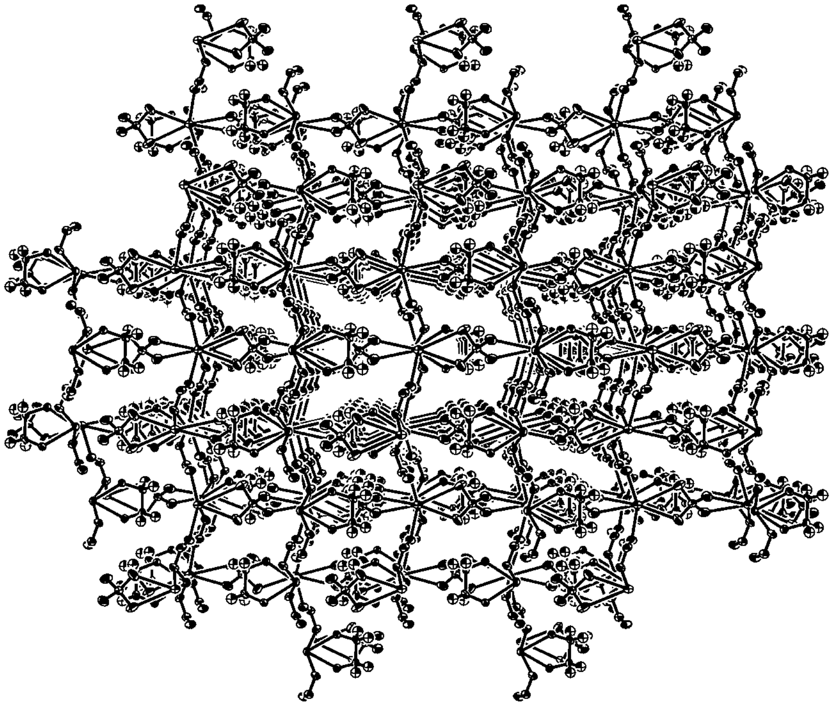

Fig. 3. *Crystal packing of* $[NaPb(ClO_4)(en)(NO_2)_2]_n$ *along the* a *axis*

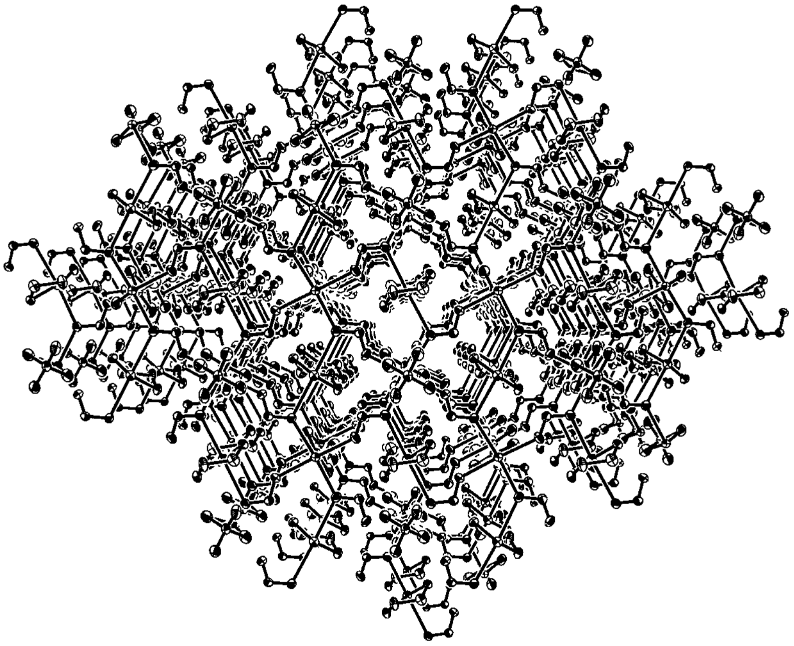

Fig. 4. *Crystal packing of* $[NaPb(ClO_4)(en)(NO_2)_2]_n$ *along the* c *axis*

ligand atoms are directed throughout the surface of an encompassing sphere, while hemidirected refers to those cases in which the bonds to ligand atoms are directed throughout only part of the coordination sphere, leaving a gap in the distribution of bonds to the ligand. The latter, present in all Pb^{II} compounds with coordination number 2 to 5, is quite common in Pb^{II} compounds with coordination numbers 6, 7, and 8, and does not exist in Pb-complexes with higher coordination numbers, in the latter cases holodirected geometry is the rule. For the structure described here, coordination around the Pb-atoms is hemidirected.

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REFERENCES

[1] B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629.

[2] M. Brian, Z. J. Michael, *Chem. Rev.* **2001**, *101*, 1629.

[3] D. Braga, F. Grepioni, G. R. Desiraju, *Chem. Rev.* **1998**, *98*, 1375.

[4] M. Fujita, O. Sasaki, T. Mitsuhashi, T. Fujita, J. Yazaki, K. Yamaguchi, K. Ogura, *Chem. Commun.* **1996**, 1535.

[5] J. Manna, C. J. Kuehl, J. A. Whiteford, P. J. Stang, D. C. Muddiman, S. A. Hofstadler, R. D. Smith, *J. Am. Chem. Soc.* **1997**, *119*, 11911.

[6] P. J. Stang, B. Olenyuk, *Angew. Chem., Int. Ed.* **1996**, *35*, 732.

[7] R. V. Slone, J. T. Hopp, *Inorg. Chem.* **1997**, *36*, 5422.

[8] A. Morsali, A. R. Mahjoub, *Chem. Lett.* **2003**, 65.

[9] I. Resino, M. Monfort, J. Ribas, M. F. Bardia, X. Solans, *Polyhedron* **2000**, *19*, 225.

[10] A. Gleizes, A. Mayer, M. A. Hotchman, O. Kahn, *Inorg. Chem.* **1983**, *21*, 2257.

[11] A. J. Finney, M. A. Hotchman, C. L. Raston, G. L. Rowbottom, A. H. White, *Aust. J. Chem.* **1981**, *34*, 2139.

[12] D. M. L. Goodgame, M. A. Hitchman, D. F. Marsham, P. Phavanantha, D. Rogers, *J. Chem. Soc., Dalton Trans.* **1969**, 1383.

[13] L. K. Chou, K. A. Abboud, D. R. Talham, W. W. Kim, M. W. Meisel, *Chem. Mater.* **1994**, *6*, 2051.

[14] L. Shimoni-Livny, J. P. Glusker, C. W. Bock, *Inorg. Chem.* **1998**, *37*, 1853.

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